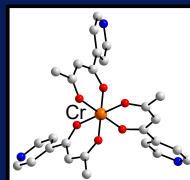


## On delineating the factors on how crystals of metal-organic species form

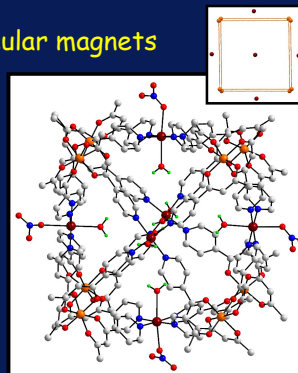
Edward R.T. Tiekink  
Research Centre for Crystalline Materials

43rd International Conference on Coordination Chemistry  
**ICCC2018 Sendai Japan**  
July 30 – August 4, 2018

## Molecular magnets

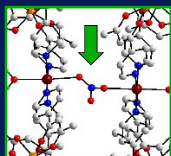
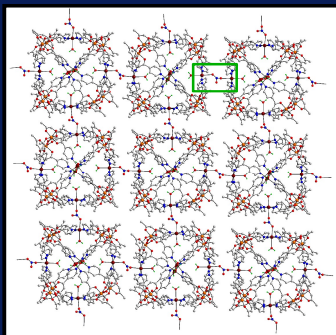


+ Cu(NO<sub>3</sub>)<sub>2</sub>



Sanz et al., *Angew. Chem., Int. Ed.* **54** (2015) 6761.

## Molecular magnets

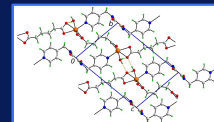


Sanz et al., *Angew. Chem., Int. Ed.* **54** (2015) 6761.

## Crystals?

Why do crystals form?

How do crystals form?

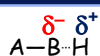


## Molecular packing

Well known...

Hydrogen-bonding (HB)  
Halogen-bonding (HB)

(HB)<sup>2</sup>: Similar in energy = 5 - 15 kcal/mol

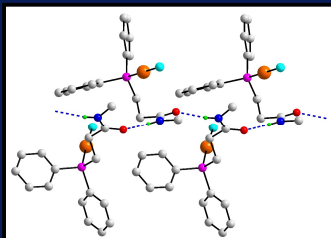
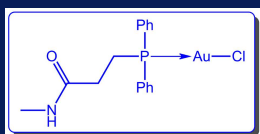


## Molecular packing

(HB)<sup>2</sup>: Similar in energy = 5 - 15 kcal/mol

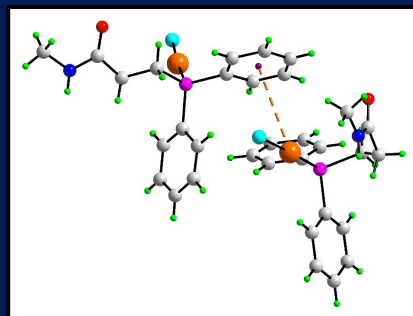
Do not always form

May not extend in 3-D



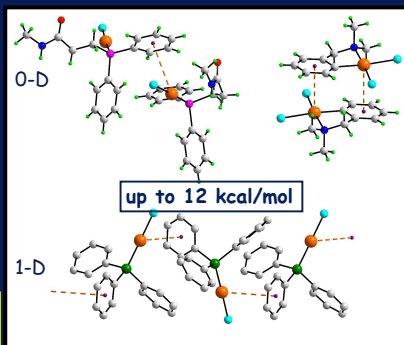
Schmidbaur et al., *Inorg. Chem.* **35** (1996) 637; *Coord. Chem. Rev.* **275** (2014) 130.

## Intermolecular Au...π(arene) interactions



*CrystEngComm* **11** (2009) 1176; *Gold Bull.* **46** (2013) 81.

## Intermolecular Au...π(arene) interactions



*RSC Advances* **5** (2015) 41401.

## Gold Chemistry

Competition between

- i) Au...Au and hydrogen bonding

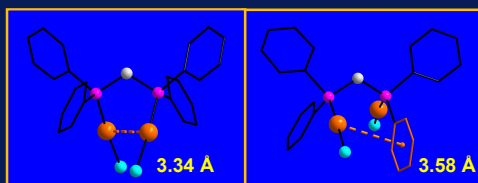


Comparable in energy to hydrogen bonding

Schmidbaur, *Nature* **413** (2001) 31.



## Polymorphs of (dppm)(AuCl)<sub>2</sub>



Schmidbaur et al. *Chem. Ber.* **110** (1977) 1748;  
Healy, *Acta Crystallogr. E* **59** (2003) m1112.

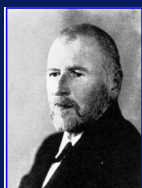
## Gold Chemistry

Competition between

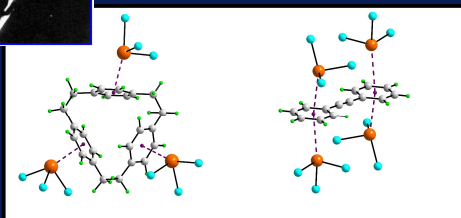
- i) Au...Au and hydrogen bonding
- ii) Au...Au and Au...π(arene)

(HB)<sup>2</sup>: Similar in energy = 5 - 15 kcal/mol

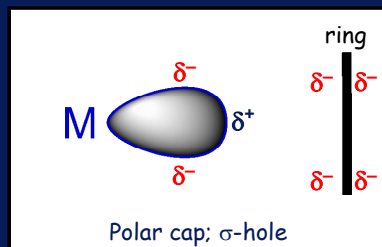
## Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



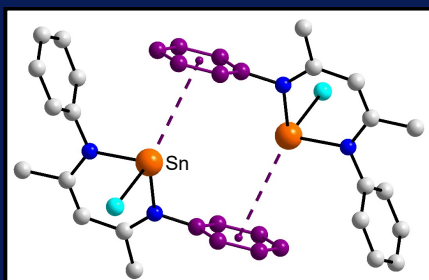
"Menšutkin complexes"



## $M(\text{lone-pair}) \cdots \pi(\text{arene})$ interactions?

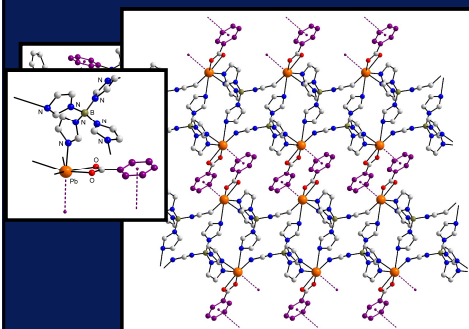


## Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



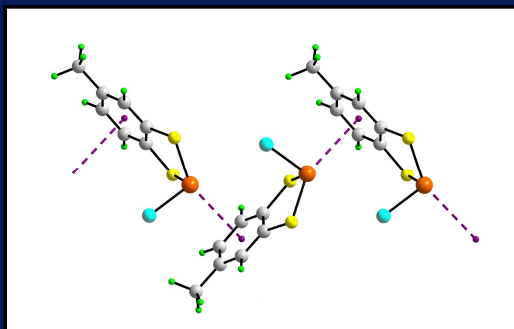
*Tin Chemistry: Fundamentals, Frontiers and Applications* (2008) Chp. 3

## Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



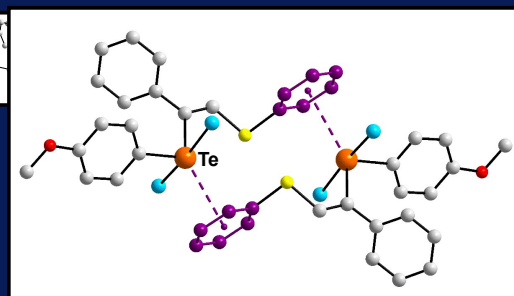
*Aust. J. Chem.* **63** (2010) 535.

## Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



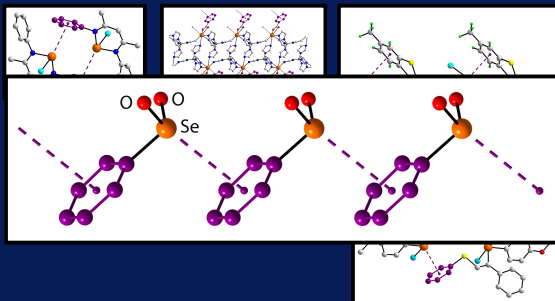
*Chem. Commun.* **47** (2011) 7608.

## Intermolecular $M(lp) \cdots \pi(\text{arene})$ interactions



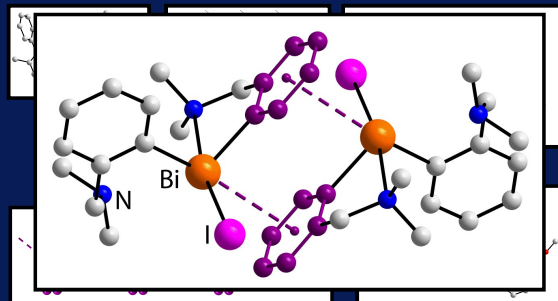
*Frontiers in Crystal Engineering II*, (2012) Ch. 12.

### Intermolecular M(lp)··· $\pi$ (arene) interactions



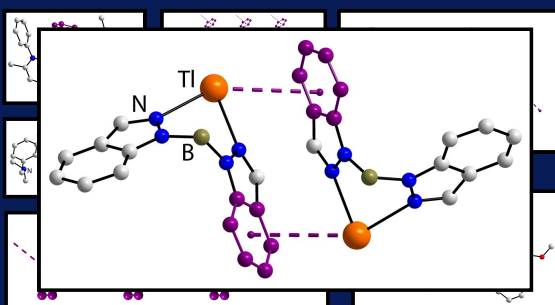
*Coord. Chem. Rev.* **256** (2012) 412.

### Intermolecular M(lp)··· $\pi$ (arene) interactions



*Coord. Chem. Rev.* **257** (2013) 2863.

### Intermolecular M(lp)··· $\pi$ (arene) interactions



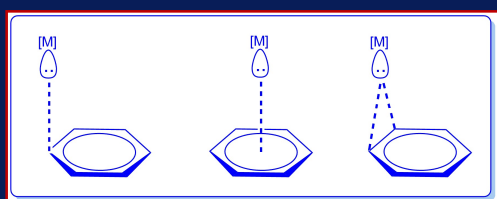
*Coord. Chem. Rev.* **281** (2014) 50.

### Prevalence?

Tl: 14%

### Tl(lp)··· $\pi$ (arene) Interactions, CSD Search

Search protocols:  $\alpha < 30^\circ$

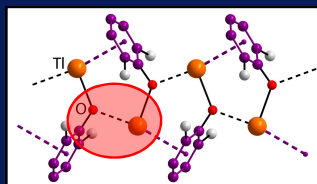


localised

delocalised

semi-localised

### Tl(lone pair)··· $\pi$ (arene) Interactions



$d = 3.16 \text{ \AA}$ ,  $\alpha = 4.2^\circ$

Excluded, as Tl(lp)··· $\pi$  not operating in isolation

## Prevalence?

Tl: 14%

Delocalised/Semi-localised/Localised

Cooperativity

{Au: x7 probability of Au-C}

## Energy?

ChemComm

COMMUNICATION



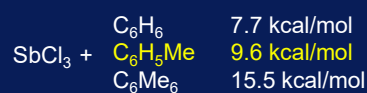
View Article Online  
View Journal | View Issue



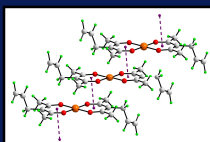
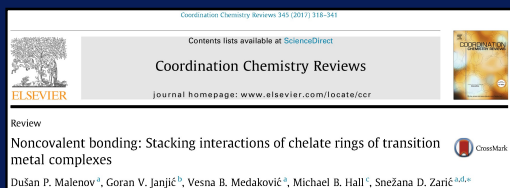
Cite this: Chem. Commun., 2016,  
52, 3500.  
Received 17th December 2015,  
Accepted 27th January 2016  
DOI: 10.1039/C5CC03638K

On the nature of the stabilisation of the E... $\pi$   
pnictogen bond in the  $\text{SbCl}_3 \cdots \text{toluene}$  complex†

Rabindranath Lo,<sup>a</sup> Petr Švec,<sup>b</sup> Zdeňka Růžicková,<sup>b</sup> Aleš Růžička<sup>b</sup> and  
Pavel Hobza<sup>a,c</sup>



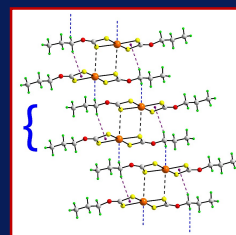
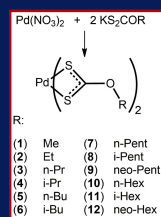
## $\pi(\text{chelate}) \cdots \pi(\text{chelate})$ interactions



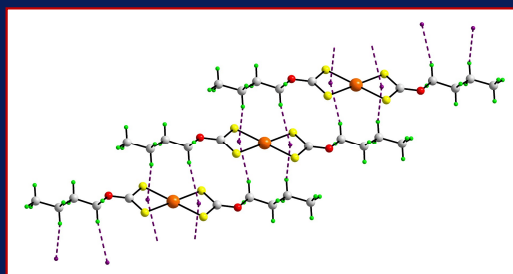
$\pi(\text{chelate}) \cdots \pi(\text{arene}) \sim 6 \text{ kcal/mol}$

$\pi(\text{chelate}) \cdots \pi(\text{chelate}) \sim 9 \text{ kcal/mol}$

## C—H... $\pi(\text{chelate})$ interactions:



## C—H... $\pi(\text{chelate})$ interactions:



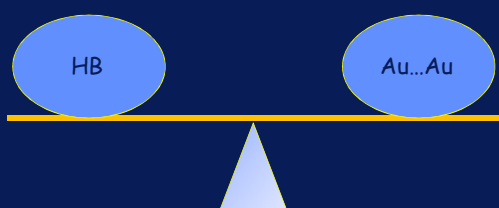
## Intermolecular interactions involving chelate rings



$\text{Pd} \cdots \text{S}$	16 kcal/mol
$\text{C-H} \cdots \pi(\text{chelate})$	15 kcal/mol

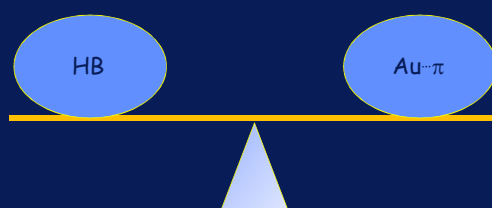
### Conclusions

More to supramolecular life than  $(\text{HB})^2$   
"Emerging" interactions are competitive  
Global molecular packing



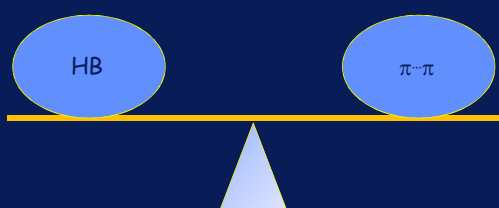
### Conclusions

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Global molecular packing



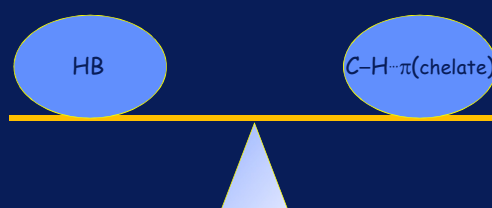
### Conclusions

More to supramolecular life than  $(\text{HB})^2$   
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Global molecular packing



### Conclusions

More to supramolecular life than  $(\text{HB})^2$   
"Emerging" interactions are competitive  
Global molecular packing



### Sunway University



EDUCATION GROUP  
SUNWAY UNIVERSITY  
SUNWAY CAMPUS  
KUALA LUMPUR

Fortuna Eruditis Favet ("Fortune favours the prepared mind")

### Announcement



7<sup>th</sup> Asian Conference on Coordination Chemistry (ACCC7)  
15-18<sup>th</sup> October 2019 / Kuala Lumpur, Malaysia

<https://www.accc7.org.my/>